

NICOTINE AS A PRECIPITANT FOR CERTAIN METALLIC IONS
IN INORGANIC QUALITATIVE ANALYSIS

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I. INTRODUCTION

In the belief that the use of certain organic reagents might offer distinct advantages over the older, more familiar inorganic reagents in the precipitation and identification of the metallic ions, many investigators have, in recent years, explored the field of organic chemistry.

The most commonly used method for the separation and identification of the metallic ions is that devised by A.A. Noyes, late Professor of Chemistry of the California Institute of Technology. Because it requires the use of gaseous hydrogen sulfide as a precipitating agent in its principal separations, the Noyes method offers many disadvantages. In addition to being an inefficient precipitant because of its gaseous nature and its low solubility, hydrogen sulfide is quite toxic and possesses a very unpleasant odor. The value of this method as an instrument for teaching the practice and theory of qualitative analysis, however, is unquestioned.

Many schemes have been developed in which the objectionable features common to the use of hydrogen sulfide have been overcome. Most of these schemes have effected a separ-

ation by a regrouping of the metals on the basis of the solubilities of their salts and their amphoteric and complex-forming properties. Other methods which have been suggested precipitate many of the metals as sulfides, without the attendant disadvantages of gaseous hydrogen sulfide, by the use of thio-acids, principally thioacetic acid.

The advantages and opportunities available in the use of organic compounds as reagents in the qualitative determination of the metals are many. This has been evident since the early applications of organic substances in the identification of metals, namely, α -nitroso-B-naphthol and dimethylglyoxime as tests for cobalt and nickel, respectively. Introduced as an analytical reagent in 1885 by M. Ilinsky and G. Von Knorre, the former is still in common use, while the latter, which was first used by L. Tschugaeff in 1905, has been shown to be one of the most accurate tests yet suggested for the detection of nickel. Later work with other organic compounds served to establish the value of this class of substances as reagents in chemical analysis. No longer was the solution medium confined to water. In the organic field the number of solvent possibilities is great, with so many alcohols, ethers, ketones and other solvents available. Also, by modification of the pH of a solution, the use of organic reagents often permits formerly difficult separations to be accomplished with comparative ease. An almost unlimited number and variety of organic compounds

affords the analytical chemist an excellent source of superior reagents. Thus far, more than six hundred carbon compounds have been suggested as analytical reagents.¹

Numerous schematic systems have been developed using these compounds both as group precipitants or as confirmatory reagents. Among these schemes is that advanced by H. L. Edwards, J. T. Dobbins and E. C. Markham, of the University of North Carolina.² In this method, the silver group remains unchanged, while the heavy metals are precipitated by a pyridine-thiocyanate reagent, and the alkaline earths are separated by ammonium carbonate precipitation. Organic reagents are employed in the detection of the individual metallic ions in their respective groupings.

The behavior of pyridine with the heavy metals in forming complexes which may be precipitated by the addition of thiocyanate ions has prompted the present investigation. In this study a number of derivatives of pyridine were investigated with the purpose of determining the effect of the substitution of various constituent groups on the pyridine ring in so far as their value as analytical reagents is concerned. For the most part, the introduction of a supplementary grouping appeared to alter completely the analytical

¹Yoe, J. H., and Sarver, L. A., Organic Analytical Reagents (New York: Wiley and Sons, 1941), p I.

²Dobbins, Markham and Edwards, J. Chem. Education, 16: 94-98, February, 1939.

properties of the parent compound, pyridine. With the exception of nicotine, or 1-methyl-2-[3-pyridyl]-pyrrolidine, none of the derivatives studied gave any indications of noteworthy analytical possibilities other than a few none-too-reliable tests. In addition to those derivatives, more than thirty other compounds were studied under varying conditions to determine their value as reagents in qualitative analysis.

A new scheme of analysis has been developed using nicotine in the presence of the thiocyanate ion as a group reagent for the precipitation of the heavy metals, and using various other organic compounds as confirmatory reagents in the final identification of these metals. This method offers a rapid and rather simple means of analysis which is found to have numerous advantages over the older, more common scheme. Although the procedure has been developed according to semi-micro techniques, the reader will find that ordinary macro methods can be employed equally as well.

II. THEORETICAL DISCUSSION

The classical valence theory offers a satisfactory explanation for the formation of first order compounds, which may be recognized by the fact that their atomic affinity, or valence, is satisfied. Frequently, however, stable compounds of the first order combine with each other to form new stable compounds of higher order. For example, the molecule $\text{Fe}(\text{CN})_3$ can combine with three molecules of KCN and thus form the new stable compound $\text{K}_3\text{Fe}(\text{CN})_6$, the properties of which differ completely from those of the basic constituents. This compound dissociates into K^+ and $\text{Fe}(\text{CN})_6^{=}$ in aqueous solution. If the ordinary valences of the atoms are retained, it is found that attempts to formulate such compounds meet with no success.

In 1891, Alfred Werner advanced an explanation for the fact that certain atoms or molecules, usually regarded as being completely saturated, still retain a combining power sufficient to attach to themselves other atoms or molecules. Werner's coordination theory introducing the concept of auxiliary or secondary valence is today generally accepted, although it was at first slow in gaining acceptance because of its lack of theoretical basis. According to his theory, certain atoms possess, besides the affinity as expressed in the valence, an additional affinity, known as the "covalence."

The inorganic complex compounds consist of an inner, or central, atom around which are grouped a number of attached atoms or groups, the number of which is determined primarily by stereochemical considerations. Attached by auxiliary, or secondary, valence forces, these radicals are called "coordinated groups" by Werner, and their number designated as the "coordination number." The maximum coordination number determines how many groups it is possible for the central atom to hold. For most metals this number is six, and for non-metals it is four, although complexes do exist in which it is eight.

The nature of the radicals or molecules attached to the inner atom bears no relation to the coordination number; that is, its magnitude is the same whether neutral water molecules, acid radicals (e.g., Cl^- , Br^- , CN^- , etc.), hydroxyl groups, oxygen atoms or ammonia molecules are present. Only one coordination position may be occupied by any one of these groups.

The tendency to act as the inner atom of a complex nucleus generally increases with diminishing electric potential. This is shown by the fact that very few of the alkali metals, which are uppermost in the electromotive series, form complex compounds; while most of the compounds of the noble metals, found at the bottom of the series, are of a complex nature.

On the basis of the Werner system, inorganic complex compounds are classified as three main types: addition compounds, penetration or intercalation compounds, and inner complex compounds.

Compounds of the addition type are characterized by the fact that the direct union between the anion and cation is not changed in the solid or dissolved state. An example of an addition compound is that formed by pyridine and chromic chloride, $\text{CrCl}_3 \cdot 3\text{Py}$ (where Py represents pyridine, $\text{C}_5\text{H}_5\text{N}$). Such compounds do not usually exhibit electrolytic properties.

In the penetration compounds, the added neutral groups enter between (i.e., penetrate) the cation functioning as the inner atom and the anion, thus serving to loosen the bond between the cationic and anionic constituents. The deep blue colored copper tetrammine sulfate illustrates the penetration type: $\text{Cu}(\text{NH}_3)_4\text{SO}_4$. It will be noted that only the NH_3 molecules, and not the SO_4^- ion, are bound to the copper ion in a complex linkage.

A metallic or non-metallic ion linked coordinately to a different atom of the same molecule forms a compound of the inner complex type. In such compounds, the metal forms a heterocyclic ring in fulfilling the principal and covalences, observing the same rules which govern the rings united by principal valences only. The nickel-dimethylglyoxime is probably the best known example of an inner complex compound.

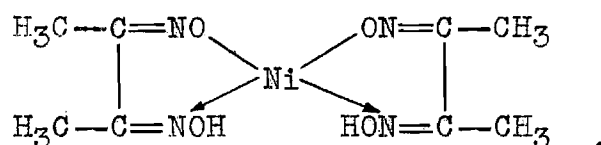
Organic reagents are generally classified according to their various peculiarities of structure and their functional groups. Most common of the important types include: (a) salt-forming substances; (b) substances forming addition compounds which are either characteristically colored or insoluble; (c) organic syntheses in which the substance to be tested reacts with the reagent to form a new compound; (d) substances which are capable of forming highly colored complexes; (e) adsorption-complex forming dyes; (f) oxidizing and reducing agents; and (g) reagents possessing a composition which forms a ring structure with metals by means of two coordinate valences, or by two electrovalences, or by one coordinate valence and one electrovalence.

The salt-forming group includes those compounds which can unite with metals through the displacement of the acidic hydrogen. The metal is held in the resulting compound by a primary valence. Still other reagents possess groups which have the power of combining with metals by the coordination bond without the displacement of hydrogen.

Those cyclic structures resulting from the union of certain organic reagents have been termed "chelate compounds" by Morgan.¹ Primary and secondary valences play a role in a combination of this nature. The metallic ions are secured in position by two electrovalences, or by one electrovalence

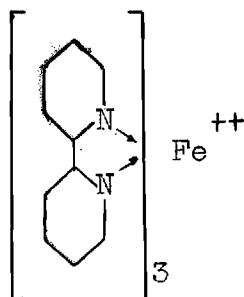
¹Morgan, G.T., and Drew, H.D.K., J. Chem. Soc., 117: 1456 (1920).

and one coordinate valence, or by two coordinate valences. The cyclic structures formed usually consist of six atoms having two, one, or no double bonds, or five atoms possessing one or no double bonds. Reactions in which eight, seven, four and three membered rings are formed are known, but such structures are not nearly so stable as those of five and six members. In chelate rings the metal is usually attached to a nitrogen, oxygen or sulfur atom, and it completes the ring through coordinate valence. The nickel-dimethylglyoxime compound will illustrate the chelate type:



As a rule, chelate compounds are characterized by their colors, insolubility in water and solubility in non-polar solvents.

Highly colored coordination compounds are produced by the reaction between certain organic reagents and inorganic ions. The intense red colored addition compound formed by a,a'-dipyridyl with ferrous iron illustrates this type:

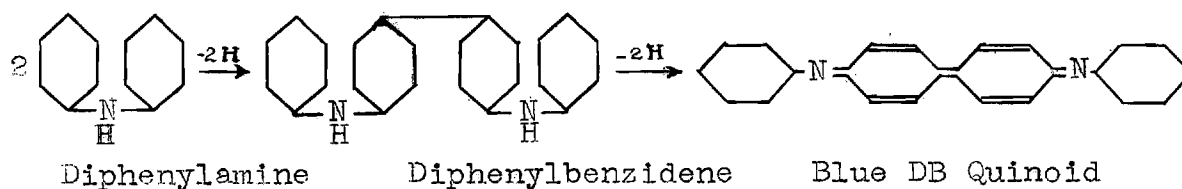


There are other organic reagents capable of forming colored metal complexes which are soluble in organic solvents, or water, and which impart to the solution an intensity of coloration which is proportional to the quantity of the metal complex present.

Crystalline compounds of high molecular weight formed in an organic synthesis make certain other organic substances valuable as reagents. Only a small amount of the metal ion need be present in order to cause precipitation, because the percentage of metal in the crystalline compound is so small.

Adsorption complexes are formed by combinations of organic components by auxiliary valences in ratios which are not stoichiometric. An example of an adsorption complex, also known as a "lake," is that formed by aluminum with the ammonium salt of aurintricarboxylic acid, or "aluminon."

Many organic compounds are readily oxidized or reduced by certain metals, or conversely, the organic substances act as reducing or oxidizing agents. In undergoing this change, characteristic colors are often formed. Colorless diphenylamine, for example, acts as a reducing agent in reacting with ferric iron, and is oxidized to diphenylbenzidine, also colorless, which is further oxidized to a quinoid structure, according to the given reaction:



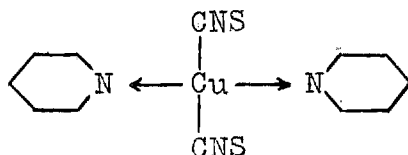
A green meriquinoid results rapidly, however, when the unstable blue oxidation product reacts with more diphenylbenzidine.²

Pyridine reacts with certain metals forming coordination compounds. The group accounting for this property is the cyclic tertiary amino group, N , which forms addition compounds because it possesses residual or secondary valence forces. The analytical value of pyridine may be attributed to four outstanding properties.³ (1) It is sufficiently basic in aqueous solution to cause precipitation of the insoluble hydroxides of aluminum, antimony, bismuth, chromium, lead and tin. Yet its aqueous solution is not basic enough to precipitate the more soluble hydroxides of cadmium, cobalt, copper, manganese, nickel and zinc. The amphoteric hydroxides of aluminum, antimony, chromium, lead and tin, however, are not dissolved by the basic reagent. (2) Pyridine is capable of forming complexes with certain metallic ions, cadmium, cobalt, copper, manganese, nickel and zinc. (3) The complex ions thus formed with these metals combine with the thiocyanate ion to precipitate insoluble compounds which have the general formula of $\text{M}(\text{CNS})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$, where M represents a

²Kolthoff and Noponen, J. Am. Chem. Soc., 55: 1448 (1933).

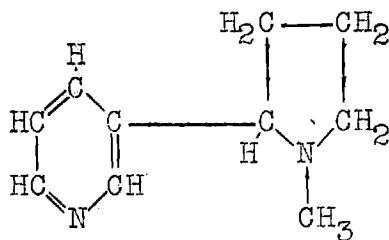
³Dobbins, Markham and Edwards, loc cit.

divalent metal.⁴ The compound formed with the copper ion may be represented as follows:



(4) These compounds are decomposed by ammonia, which converts the inner metallic ions into the corresponding soluble ammonia complexes. In the case of manganese, however, the metal is oxidized and precipitates as hydrous manganese dioxide on treatment with ammonium hydroxide. Thus, the ions of cadmium, cobalt, copper, nickel and zinc may be separated from the other heavy metals which have been precipitated as hydroxides by the pyridine-thiocyanate reagent.

Nicotine has been found by this investigation to possess properties which are in many respects analogous to those of pyridine. In aqueous solution nicotine gives a reaction which is slightly more alkaline than that of pyridine. The structure of nicotine,



⁴Mellan, Organic Reagents in Inorganic Analysis, (Philadelphia: Blakiston, 1941), p 179.

shows the presence of a methyl-pyrrolidine group in combination with the pyridyl base. Two basic nitrogen groups, therefore, account for the greater alkaline strength of nicotine. The ionization constant for pyridine is 1.4×10^{-9} , according to Kolthoff and Bosch,⁵ while the primary and secondary ionization constants for nicotine are 7×10^{-7} and 1.4×10^{-11} , according to Liquier.⁶ The first basic function is that of the pyrrolidine nitrogen, the second is that of the pyridyl nitrogen.

In aqueous solution, the insoluble hydroxides of all the heavy metals except cadmium, cobalt, copper, nickel and zinc are precipitated by nicotine. It is noted that nicotine differs from pyridine in that it causes precipitation of the slightly soluble manganese hydroxide. Yet, nicotine is not sufficiently basic to dissolve the amphoteric hydroxides of aluminum, antimony, chromium and lead.

By reason of its two active nitrogen groupings, nicotine possesses the property of forming complexes with several metallic ions, including all of those with which pyridine is known to form complexes, except manganese. FitzGibbon, working on insecticides, found that cobalt, copper, divalent mercury, nickel, tin and zinc unite with nicotine in complexes

⁵Kolthoff, I.M., and Bosch, W., Rec. trav. chim., 48: 37-48 (1929).

⁶Liquier, Ann. phys., 8: 121-203 (1927).

which form insoluble compounds with iodide, selenocyanate, cyanide and thiocyanate ions.⁷ Results of the present investigation would seem to indicate that the same course of reaction is true also for the cadmium ion. Similar to the pyridine-thiocyanate complexes, the insoluble nicotine-thiocyanate compounds are decomposed by reaction with ammonia. The inner ions of cadmium, cobalt, copper, nickel and zinc go into solution as the soluble ammonia complexes on this treatment. The tin and mercury compounds, however, are oxidized and precipitated as hydroxides, although the tin appears to form a hydrous oxide which tests show to be soluble only in concentrated sulfuric acid, and then but slightly.

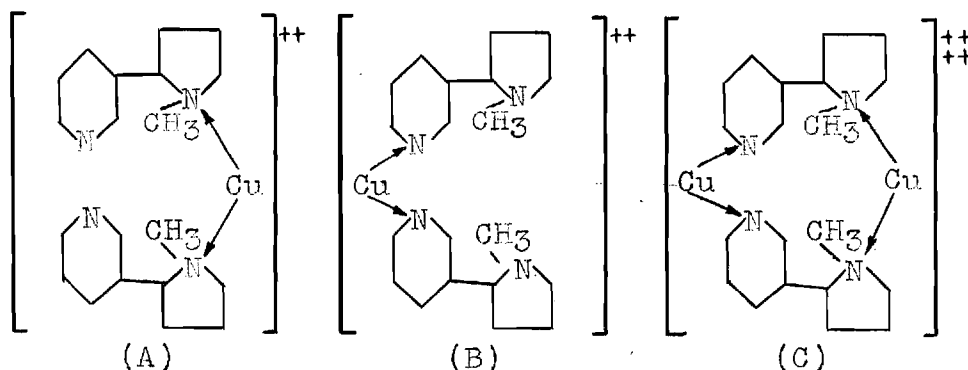
On the basis of these properties of nicotine and on the amphotericity of the hydroxides of aluminum, antimony, chromium and lead, the present method of separation of the heavy metals has been developed.

Little definite knowledge is known as to the structure of the complexes formed with nicotine. Both basic constituents of nicotine, i.e., pyrrole and pyridine, are known to enter into complexes with certain metallic ions. Whether the pyridyl nitrogen or the pyrrolidine nitrogen is the active grouping in the complex forming reaction is not known at present. It is very unlikely, however, that both groupings are responsible for such reactions. Space models of

⁷FitzGibbon, M., British Patent 492,660 (9/20/38).

nicotine show no reasonable possibilities of an inner complex or chelate ring involving both nitrogen atoms. The formation of a six membered ring of this type appears impossible because of the exceedingly great strain which would be necessary.

The structures listed below are advanced by the author as possible configurations for the complexes, using copper as the metallic ion. When precipitated, these complexes would



be represented by the following formulas: $A(CNS)_2$, $B(CNS)_2$ and $C(CNS)_4$. It is readily seen that since the metallic ion constitutes such a small percentage of the whole molecule, only a small amount of that ion need be present to effect precipitation. For this reason, probably, the nicotine-thiocyanate reagent is an efficient group precipitant.

III. THE PRESENT SCHEME

As in all methods of qualitative analysis, it has been found advantageous in the present procedure to effect the separation of the metallic ions into a number of smaller groups. This division is accomplished by the use of several group reagents, and the individual constituents are identified in the various groupings by the use of a number of organic reagents which have been found by this investigation to be sufficiently specific in their reactions to make them suitable for the purpose.

The ordinary First, or Silver, Group has been unaltered in the course of the present scheme. This separation of the cations silver, lead and univalent mercury as insoluble chlorides, and their subsequent identification has long proved satisfactory as a rapid, accurate and relatively simple method. It was deemed unwise, therefore, to attempt further improvement upon it.

Following the removal of the insoluble chlorides, the solution is boiled with concentrated nitric acid in order to oxidize arsenic, tin, iron and antimony to their higher states of valence. In a small portion of this solution, a test is made for the identification of arsenic. Similar to the scheme of Edwards, Dobbins and Markham employing the pyridine-thiocyanate reagent, the removal of arsenates and phosphates is unnecessary since these anions do not precip-

itate the alkaline earths prematurely and, therefore, offer no interference. An optional test for divalent mercury may also be made at this point.

In the further separation of the metals, the solution is carefully neutralized with ammonium hydroxide preparatory to the precipitation of the heavy metals of Groups III and IV by the nicotine-thiocyanate reagent. The metals of the nicotine-thiocyanate group include copper, cadmium, nickel, cobalt, zinc, lead, antimony, aluminum, chromium, bismuth, divalent mercury, manganese and ferric iron.

Advantage is taken of the ammonia complex-forming properties of copper, cadmium, nickel, cobalt and zinc in effecting a further division of the third group constituents. Treatment of the water insoluble precipitates with concentrated ammonium hydroxide serves to extract all of those metals which are capable of forming the ammino complexes under ordinary conditions. Thus separated, these metals are designated as Group IV-A, or the Ammonia Complex Group.

The precipitate remaining after the extraction of Group IV-A is further separated on the basis of amphoteric properties of the metals lead, antimony, aluminum and chromium. These metals, which are brought into solution as plumbate, antimonite, aluminate and chromite ions by a hot sodium hydroxide solution, form Group IV-B, or the Amphoteric Group.

Solution of the residue from the previous sodium

hydroxide treatment is accomplished with hot nitric acid, which will dissolve the hydroxides of bismuth, divalent mercury, manganese and ferric iron to give Division A of Group III, the Iron-Tin Group. Any grayish colored insoluble residue remaining after careful treatment according to the foregoing procedure may be considered to be tin. Concentrated sulfuric acid was found to dissolve a sufficient amount of this stannic residue to produce a satisfactory test for tin.

Group V, comprising the alkaline earths, is precipitated as in the older schemes by the addition of ammonium carbonate solution to the filtrate remaining after the precipitation of Groups III and IV by the nicotine-thiocyanate reagent. With barium, strontium and calcium thus removed, the final filtrate contains magnesium and the alkalies sodium, potassium and ammonium. For obvious reasons, the test for ammonium must be made on a portion of the original solution, rather than on the filtrate from Group V.

In the event that the color of the original solution should suggest the probable presence of either chromate or permanganate ions, these may be reduced to chromic and manganous ions by treatment with nitric acid and hydrogen peroxide. A colorless solution will indicate the absence of both of these ions and the hydrogen peroxide treatment will not be necessary.

Organic reagents are further employed in the identification of the various cations in their respective groups.

Tests for the metallic ions have been devised which may be utilized directly with the different group solutions, thereby reducing to a minimum the number of individual separations necessary in carrying out the analysis.

At present it is not possible to explain all of the reactions which make the organic compounds used in this procedure so valuable as analytical reagents. Nor is it possible to give formulas for all of the complex metallo-organic compounds resulting from these reactions, but examples will be supplied in those cases for which analogous reactions have been advanced and formulas definitely determined. In many instances, the metal will be attached to the organic compound either by electrovalent or covalent linkages, or some combination of these. The metal serves in the capacity of an oxidizing agent in reacting with some other compounds and causes an internal rearrangement in the organic molecule which produces a characteristic result. Some other metals are linked to the organic base by covalent bonds and require the addition of a negative ion or group to effect precipitation, such as is probably the case in the nicotine-thiocyanate precipitates.

The application of semimicro techniques in following this procedure offers a considerable saving in the amounts and costs of materials and in the time required, as well. While several of the organic compounds used in the scheme may be relatively expensive, the minute amounts needed serve

to lessen this cost to a large extent. Throughout the investigation advantage is taken of the increase in sensitivities of numerous tests brought about through capillary phenomena by carrying out reactions on impregnated filter paper spot plates wherever such procedure is feasible. Drop reactions as tests are also performed on porcelain spot plates when practicable. The semimicro method, in replacing the slow ordinary filtrations by the much more rapid centrifugation, enables the separation of the precipitates to be accomplished effectively in considerably less time. By this process, too, a large part of the procedure may be carried out in the same tube, which makes negligible the loss of precipitate usually incurred in transference and by the use of filter paper in the ordinary separation. Macro methods may, of course, be used in following the present scheme when a centrifuge or semimicro equipment is not available to the analyst.

CHART I: GENERAL SCHEME OF ANALYSIS

The solution containing all of the metals in the form of salts is acidified with HNO_3 . If color of solution suggests the presence of $\text{CrO}_4^{=}$ or MnO_4^- , add H_2O_2 and boil to reduce to Cr^{++} and Mn^{++} . Add HCl to complete pptn. Filter.			
Residue: Group I.	Filtrate: Groups II-VI. Add conc HNO_3 and boil to oxidize As^{+++} , Fe^{++} , Sb^{+++} and Sn^{++} . Remove two small portions of soln to test for Group II.		
AgCl , PbCl_2 , Hg_2Cl_2 . Treat as directed in Section 2.	Group II: Test one portion for As^{+++} . Add ammonium molybdate. Yellow ppt confirms presence of As^{+++} .	Remainder of soln is made just alkaline with NH_4OH and then HCl is added until neutral or very slightly acid. Add nicotine-thiocyanate reagent until pptn is complete. Filter.	
		Residue: Groups III-IV. Cu^{++} , Cd^{++} , Ni^{++} , Co^{++} , Zn^{++} , Sn^{+++} , Hg^{++} as nicotine-CNS complexes. Bi^{+++} , Fe^{++} , Sb^{+++} , Al^{+++} , Cr^{+++} , Mn^{+++} , Pb^{++} as hydroxides.	Filtrate: Groups V-VI. Add 1 g NH_4Cl , make alkaline with NH_4OH , then add $(\text{NH}_4)_2\text{CO}_3$ and heat. Filter.
		Residue: Group V. Ba^{++} , Sr^{++} , Ca^{++} as carbonates. Treat according to Section 7.	Filtrate: Group VI. Contains Mg^{++} , Na^{+} , K^{+} , NH_4^{+} . Identify by Section 8.
To the second portion add SnCl_2 . Formation of a white ppt turning gray indicates Hg^{++} .			
Add NH_4OH and stir well. Filter.			
Filtrate: Group IV-A. Cu^{++} , Cd^{++} , Ni^{++} , Co^{++} , Zn^{++} as NH_3 complexes. Analyze according to Section 6A.	Residue: Groups III and IV-B. Add NaOH and heat. Filter.		
	Filtrate: Group IV-B. AlO_2^- , CrO_2^- , PbO_2^- , $\text{SbO}_4^{=}$. Treat as shown in Section 6B.	Residue: Group III. Add HNO_3 ; heat and filter.	
		Filtrate: Group III-A. Bi^{+++} , Fe^{++} , Mn^{++} , Hg^{++} as soluble nitrates. Test as directed in Section 5A.	Residue: Group III-B. A grayish white residue indicates Sn^{+++} . Treats according to Section 5B.

IV. LABORATORY PROCEDURE

Section 1. PREPARATION OF THE SOLUTION FOR ANALYSIS

A quantity of material containing approximately 50 mg of each metallic ion is used for the analysis. If the substance is water-soluble, it is dissolved in 20 ml of water. If insoluble, the material is brought into solution in the appropriate acid, the solution evaporated almost to dryness, and 20 ml of water added to the residue. A small amount of nitric acid may be added when necessary to prevent hydrolysis.

A yellow or purplish tinted solution may contain chromate or permanganate ions. These must be reduced to the chromic and manganous ions, respectively, by treating the acid solution with 3 ml of 3 per cent hydrogen peroxide and heating on a boiling water bath for three to five minutes. The absence of both chromate and permanganate ions is indicated when the solution is colorless, and the hydrogen peroxide treatment is unnecessary. The solution is now ready for the removal of Group I and the subsequent treatment according to Section 2.

Section 2. SEPARATION AND ANALYSIS OF GROUP I

To the solution prepared as directed in Section 1, 3N hydrochloric acid is added slowly until one drop gives no evidence of further precipitation. The formation of a

CHART II: SCHEME OF ANALYSIS FOR GROUP I

A white residue remaining after the HCl treatment may consist of AgCl , PbCl_2 and Hg_2Cl_2 . Wash the ppt with 2 ml of H_2O containing HCl, and reject the washings. Add 3 ml of hot H_2O to residue in tube, mix well, centrifuge, and decant clear soln while hot. Repeat with another 3-ml portion; combine the solns in a test tube to test for Pb^{++} .

Solution: May contain PbCl_2 . Add 1 ml dilute HOAc and then 1 ml of K_2CrO_4 soln. A yellow ppt confirms presence of Pb^{++} .

Residue: May be AgCl and Hg_2Cl_2 . If a positive test for Pb^{++} has been obtained, the residue must be washed with small portions of hot water until the washings yield no ppt with K_2CrO_4 . To the residue in a tube, add 5 ml NH_4OH , shake well, centrifuge, and decant off clear soln.

Solution: May contain $\text{Ag}(\text{NH}_3)_2^+$. Acidify with dilute HNO_3 . Formation of a curdy white ppt or cloudiness indicates the presence of Ag^+ .

Residue: If black, the presence of Hg_2^{++} is indicated. To confirm, dissolve in 2 ml of aqua regia, boil down to a few drops and add 2 ml of water. Centrifuge if necessary. Treat the soln with a few drops of a saturated soln of SnCl_2 . A white ppt turning gray proves the presence of Hg_2^{++} .

heavy white precipitate indicates the presence of silver, lead or mercury. The mixture is transferred to a tube and centrifuged until the precipitate is completely separated. If a centrifuge is not available, the separation may be accomplished by filtration. By means of a dropper or a pipet, the supernatant liquid is carefully withdrawn from the tube, placed in a small flask or beaker, labelled "Groups II-VI," and set aside for later consideration according to Section 3.

The precipitate remaining in the centrifuge tube is washed by adding 2 ml of water to which has been added a milliliter of dilute hydrochloric acid, shaking thoroughly and centrifuging again. The wash liquid is decanted off and discarded. A 5-ml portion of hot water is added to the precipitate in the tube, which is then centrifuged. While still hot, the liquid is carefully withdrawn from the mixture and placed in a test tube. This treatment is repeated with another 3-ml portion of hot water, and the two extracts, which may contain lead, are combined. To this filtrate are added 1 ml of acetic acid and 1 ml of potassium chromate solution. Formation of a yellow precipitate indicates the presence of lead.

If a positive test is obtained for lead, the Group I precipitate must be washed with hot water until the washings no longer form a precipitate with potassium chromate. When this is accomplished, 5 ml of dilute ammonium hydroxide is added to the remainder of the precipitate and centrifuged.

The supernatant liquid is pipetted off, placed in a test tube, and acidified with dilute nitric acid. A white precipitate or cloudiness forming on acidification confirms the presence of silver.

A black residue remaining from the ammonia treatment may consist of a mixture of Hg and $\text{Hg}(\text{NH}_2)\text{Cl}$ and some undissolved AgCl or Ag. If decidedly black, univalent mercury is present. To confirm its presence, 2 ml of aqua regia is added to the precipitate in the tube, and the mixture gently boiled down over a low flame until only a few drops remain, in order to destroy the excess of aqua regia. Two ml of water is added to the mixture, which is filtered if necessary, and the clear solution is treated with a few drops of stannous chloride solution. A white precipitate which may turn gray or black confirms the presence of mercury.

Section 3. IDENTIFICATION OF GROUP II

To the solution labelled "Groups II-VI," 3 ml of concentrated nitric acid is added, and the solution is boiled for three to five minutes in order to oxidize to the higher valence states any arsenic, antimony, iron and tin which may be present. If mercury has been found present in Group I, five minutes' boiling may be necessary because of the negative catalytic effect of mercury in the oxidation of arsenic to the arsenate by nitric acid.¹ A 5-ml portion is extracted

¹Klemenc and Pollack, Z. anorg. allgem. Chem., 115: 131-140 (1921).

CHART III: SCHEME OF ANALYSIS FOR GROUP II

Add 3 ml of conc HNO_3 to the soln obtained from the Group I separation and boil for three to five minutes to oxidize As^{3+} , Fe^{2+} , Sb^{3+} and Sn^{2+} . Remove a 5-ml portion of soln for Group II, label remaining soln "Groups III-VI." Divide Group II soln into 2 parts, 3 ml and 2 ml.

Part 1: Arsenic. Pour the 3-ml portion into a tube containing 5 ml of hot ammonium molybdate soln. Let stand five minutes. A yellow crystalline ppt shows the presence of either arsenate or phosphate.

Part 2: Mercury. To the 2-ml portion, add 1 ml of a satd soln of SnCl_2 . A white ppt turning gray or black indicates the presence of Hg^{2+} .

Dissolve ppt in 5 ml of 6N NH_4OH , and add this soln slowly to 5 ml of AgNO_3 soln made slightly acid with HNO_3 . A chocolate-brown ppt of Ag_3AsO_4 indicates the presence of As^{3+} .

from the resulting solution for tests for Group II. The remainder of the solution is labelled "Groups III-VI" and reserved for analysis according to Section 4.

The test for arsenic, as the arsenate, is made on 3 ml of the solution extracted for Group II. This portion is added to a tube containing 5 ml of hot ammonium molybdate reagent, and the mixture allowed to stand for two or three minutes. The presence of either arsenate or phosphate is indicated by the formation of a bright yellow crystalline precipitate. The precipitate is separated by centrifuging, the supernatant liquid drained off, and the precipitate dissolved in 5 ml of 6N ammonium hydroxide. Arsenic is tested for by adding the solution slowly to 5 ml of a slightly acid solution of silver nitrate, made by combining equal portions of silver nitrate and dilute nitric acid. The presence of arsenic is confirmed by the formation of a chocolate-brown precipitate of silver arsenate.

A test for divalent mercury is made on the remainder of the Group II solution. To this solution is added, dropwise, 1 ml of a saturated stannous chloride solution. A white precipitate, turning gray or black as the amount of stannous chloride is increased, is indicative of the presence of mercury. The test for mercury at this point is optional, as a further test may be made in Group IV-A.

CHART IV: SCHEME FOR SEPARATION OF GROUPS III AND IV

The soln labelled Groups III-VI is made alkaline with dilute NH_4OH and then carefully adjusted to neutral or very slightly acid. Nicotine-thiocyanate reagent is added with stirring until pptn is complete. The mixture is centrifuged or filtered.	
Residue: Groups III-IV. May contain Cu^{++} , Cd^{++} , Ni^{++} , Co^{++} , Zn^{++} , Sn^{+++} and Hg^{++} as nicotine-thiocyanate complexes, and Al^{+++} , Bi^{+++} , Fe^{+++} , Mn^{++} , Cr^{+++} , Pb^{++} and Sb^{+++} as hydroxides. Wash with a few ml of water and discard washings. Add 5 ml of conc NH_4OH and stir well to break up any large lumps of ppt. Centrifuge.	Filtrate: Contains Groups V-VI. Label accordingly and reserve for further treatment.
Residue: Wash with 5 ml of water containing NH_4OH , centrifuge, and combine the washings with the Group IV-A soln. Then add 5 ml of 6N NaOH to the ppt, heat for three to five minutes with occasional stirring, and centrifuge to separate the ppt completely.	Filtrate: Label "Group IV-A" and set aside.
Residue: Wash with 2 ml of water and combine the washings with the Group IV-B soln. Add 5 ml of 3N HNO_3 and heat in boiling water bath, with occasional stirring, for two or three minutes. Centrifuge to separate insoluble residue.	Filtrate: Label "Group IV-B" and reserve for later analysis.
Residue: Group III-B. Repeat HNO_3 treatment above to determine solubility of ppt. If none is dissolved, a fine grayish white residue indicates Sn^{+++} .	Filtrate: Group III-A. May contain Bi^{+++} , Fe^{+++} , Mn^{++} and Hg^{++} . Treat according to Scheme III Division A.

Section 4. PRECIPITATION OF GROUPS III AND IV

Preparatory to the precipitation of Groups III and IV by the nicotine-thiocyanate reagent, it is important that the pH of the solution be very carefully adjusted. A too-alkaline solution must be avoided, since those nicotine-thiocyanate complexes which are soluble in ammonia will not be formed. The solution must not be too highly acid, for in such a medium the mildly basic nicotine cannot effect the precipitation of the insoluble hydroxides.

Dilute ammonium hydroxide is added slowly and with constant stirring to the solution containing Groups III-VI until an alkaline reaction to litmus is obtained. Then dilute hydrochloric acid is added very cautiously until the litmus just turns pink. Any precipitation which may occur at this point is disregarded. The nicotine-thiocyanate reagent is now added slowly, with constant stirring to prevent the formation of large clumps of precipitate, until precipitation is complete. A very deep blood-red color, typical of ferric thiocyanate, will be noted immediately upon the addition of the precipitant if ferric iron is present in the solution. As the addition of the reagent is continued, this coloration is dispersed, the solution becomes colorless and a grayish green precipitate is formed. The mixture is transferred to a tube and centrifuged until the precipitate has been completely separated. The clear supernatant liquid resulting from the centrifugation is withdrawn from the tube,

placed in a flask labelled "Groups V-VI," and set aside for further consideration in Section 7.

The precipitate is washed with a few milliliters of water and the washings are discarded. To the precipitate in the centrifuge tube is added 5 ml of concentrated ammonium hydroxide, and the mixture stirred well with a stirring rod, which is also used to break up any large lumps of precipitate present. The precipitate is separated by centrifuging, the ammonia solution carefully extracted and placed in a flask labelled "Group IV-A." A solution of 1 ml concentrated ammonium hydroxide and 4 ml of water is used to wash the precipitate in the tube. The washings are combined with the Group IV-A solution for treatment in Section 6A.

Five ml of 6N sodium hydroxide is added to the residue remaining from the ammonia treatment above; the mixture is stirred thoroughly, and heated in a bath of boiling water for four or five minutes with occasional stirring. The mixture is then centrifuged until the precipitate is completely separated, the clear liquid is pipetted off and transferred to a flask labelled "Group IV-B" for later treatment according to Section 6B. A 2-ml portion of water is used to wash the precipitate and the washings are added to the Group IV-B solution.

The precipitate remaining in the tube after the above treatment contains the metals of Group III. The A-Division, consisting of the metallic ions bismuth, divalent mercury,

manganese and ferric iron, is brought into solution by adding 5 ml of dilute nitric acid and heating in a boiling water bath with stirring. Any insoluble residue is separated by centrifuging, the clear solution is pipetted off, placed in a flask marked "Group III-A" and treated according to Section 5A. If the nitric acid extraction has been complete, a grayish white residue remaining after the above treatment indicates the presence of tin. To insure the complete extraction by nitric acid, the amount of residue is carefully noted, another 5-ml portion of the dilute acid is added, and the mixture stirred thoroughly. It is then heated in the water bath as before, centrifuged, and the quantity of residue now remaining compared with the amount obtained before adding the acid. If there is no noticeable change in the amount of the residue, the acid solution is discarded and the precipitate reserved for the test for tin in Section 5B.

Section 5A. IDENTIFICATION OF GROUP III-A

The acid solution labelled "Group III-A" obtained in the previous treatment may contain the ions bismuth, manganese, divalent mercury and ferric iron.

Test for Manganese: To a 4-ml portion of the solution ammonium hydroxide is added to alkaline reaction with litmus, then dilute nitric acid is added carefully, dropwise, until the solution is neutral or very slightly acid. The solution is divided into two portions. Twenty per cent pyridine rea-

CHART V: SCHEME OF ANALYSIS FOR GROUP III

DIVISION A: The acid soln "Group III-A" may contain Mn^{++} , Fe^{++} , Hg^{++} and Bi^{++} . Tests for these ions are made on separate portions of the solution.

Manganese: Make a 4-ml portion just alkaline with NH_4OH , then just neutral with HNO_3 . Divide into two parts. To one part add 20 per cent pyridine reagent in excess. Filter. Add NH_4CNS soln to filtrate. A white ppt or cloudiness indicates Mn^{++} . Place a drop of the other portion on a spot plate. Add 1 or 2 drops of $NaOH$ soln, followed immediately by 3 drops of benzidine reagent. Presence of Mn^{++} is confirmed by a deep blue color which fades.

Iron: Place 1 drop of test soln on a filter paper spot plate impregnated with diphenylamine reagent. A definite green spot confirms the presence of Fe^{++} . To a 1-ml portion of test soln, add a few drops of potassium ferrocyanide. The immediate formation of a deep blue ppt or coloration shows the presence of Fe^{++} .

Mercury: A 2-ml portion of test soln is made alkaline with NH_4OH , then just neutral with HCl . Add 10 per cent Py-CNS reagent to complete pptn. Filter. Dilute filtrate with as much water. Place 2 drops of the soln on a filter paper spot plate impregnated with diphenylcarbazone soln. A resulting violet to blue coloration confirms the presence of Hg^{++} .

Bismuth: Add 2 ml of dimethylglyoxime soln to a hot 2-ml portion of test soln, and make strongly alkaline with conc NH_4OH . A yellow to orange coloration or ppt proves presence of Bi^{++} . Color is orange in the presence of Fe^{++} , bright yellow in its absence.

DIVISION B: Dissolve as much as possible of the Group III-B residue in conc H_2SO_4 , boiling for five minutes with stirring. Centrifuge. Pour clear soln carefully into a test tube containing 5 ml of water and a clean iron nail. Boil for three minutes to reduce Sn^{+++} . Divide soln into two parts.

To one portion add dropwise 2 ml of a satd soln of Hg_2Cl_2 . A white ppt turning gray or black shows presence of Sn^{++} . Add 5 drops of naphthol yellow-S reagent to the other portion, then $NaOH$ to alkaline reaction. A pink to red color confirms the presence of Sn^{++} .

gent is added dropwise to one portion until precipitation is complete, and then a few drops in excess. The mixture is centrifuged to separate the precipitate, and the supernatant liquid is decanted into another test tube. To this liquid is added dropwise 1 ml of 10 per cent ammonium thiocyanate solution. A white precipitate or cloudiness, $\text{Mn}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_2$, indicates the presence of manganese.

Another test may be made on the second portion of the slightly acid solution. One drop of this solution is placed in the depression of a porcelain spot plate, 2 drops of dilute sodium hydroxide solution is added, followed immediately by 3 drops of benzidine solution. A resulting deep blue coloration, which soon fades, confirms the presence of manganese. The coloration formed on oxidation of benzidine is said by Schmidt and Hinderer to be a blue meriquinoid product.²

Test for Iron: One drop of the group solution is placed on a filter paper spot plate impregnated with diphenylamine reagent solution. The presence of iron is indicated by a definite greenish coloration produced in the test spot. A meriquinoid oxidation product accounts for the coloration.³ The intensity of the coloration appears to be a function of the concentration of ferric iron. As little as 2 mg of iron per liter can be detected by this test.

²Schmidt, J., and Hinderer, V., Ber., 65: 87 (1932).

³Kolthoff and Noponen, J. Am. Chem. Soc., 55: 1448 (1933).

A supplementary test may be made for iron by adding a few drops of a solution of potassium ferrocyanide to another 1-ml portion of the group solution. The immediate formation of an intense deep blue coloration or precipitate, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, proves the presence of iron.

Test for Mercury: A 2-ml portion of the group solution is made just alkaline with dilute ammonium hydroxide, and then neutral or very slightly acid with dilute hydrochloric acid. Ten per cent pyridine-thiocyanate reagent is added slowly until precipitation is complete. The precipitate is separated by centrifuging; 5 drops of the supernatant liquid, which may contain mercury as the complex mercuri-thiocyanate ion, is diluted with twice as much water. Two drops of this solution is allowed to fall on a filter paper spot plate previously impregnated with diphenylcarbazone reagent. The formation of a violet to blue coloration shows the presence of divalent mercury. The coloration is caused by the mercury complex of diphenylcarbazone, $\text{Hg}(\text{C}_6\text{H}_5\text{NNHCON:NC}_6\text{H}_5)_2$.⁴

Test for Bismuth: A 2-ml portion of the group solution is heated and an equal volume of dimethylglyoxime reagent is added. The resulting solution is then made strongly alkaline with concentrated ammonia solution. The formation of a yellow to orange precipitate of the bismuth oxime indicates the presence of bismuth. The color of the precipitate is depend-

⁴Feigl, F., Mikrochemie, 1: 12 (1923).

ent upon the results of previous tests. If iron is present, the color will be orange, while in the absence of iron, a bright yellow color is obtained.

Section 5B. IDENTIFICATION OF GROUP III-B

Test for Tin: To the precipitate designated as Group III-B, 3-4 ml of concentrated sulfuric acid is added, the solution boiled for five minutes in a water bath with occasional stirring. It is then centrifuged, the supernatant liquid decanted into a test tube containing 5 ml of water and a clean iron nail. This mixture is boiled for three to five minutes to reduce the metal to the stannous state, then filtered and the filtrate divided into two portions.

To one portion 2 ml of a saturated solution of mercuric chloride is added. A white precipitate turning gray or black is indicative of the presence of tin.

Five drops of naphthol yellow-S reagent is added to the other portion, followed by dilute sodium hydroxide solution to basic reaction. The presence of stannous tin is confirmed by the formation of a pink to red color.

Section 6A. IDENTIFICATION OF GROUP IV-A

A bluish tinge in the solution containing the ions of this group suggests the presence of either copper or nickel, or both.

Test for Nickel: To a 1-ml portion of the group solu-

CHART VI: SCHEME OF ANALYSIS FOR GROUP IV

DIVISION A: The soln of Group IV may contain Cu^{++} , Cd^{++} , Co^{++} , Ni^{++} and Zn^{++} as NH_3 complexes. A bluish coloration suggests the presence of either Cu^{++} or Ni^{++} , or both. Tests are made on individual portions of the soln.

Nickel: Add 1 ml of dimethylglyoxime reagent to 1 ml of the test soln. A bright red ppt confirms the presence of Ni^{++} .

Cobalt: Neutralize a 2-ml portion of soln with HCl and add a gram of NaOAc , then 2 ml of nitroso-R-salt soln and boil. Now add 1 ml of conc HNO_3 and boil for two minutes. A red color which persists will form in the presence of Co^{++} .

Zinc: Acidify a 3-ml portion of test soln with HOAc and then make basic with 3N NaOH , adding 1 ml in excess. Filter. Save residue for cadmium test. Add 5 drops of 8-hydroxyquinoline reagent to filtrate. A heavy yellow ppt forms if Zn^{++} is present.

Cadmium: Dissolve in HOAc the ppt from the zinc test above. Make soln basic with NH_4OH and add 8-hydroxyquinoline reagent dropwise. A heavy ppt proves presence of Cd^{++} .

Copper: A drop of test soln is placed on a filter paper spot plate, then a drop of diphenylthiocarbazone reagent is added. The presence of Cu^{++} causes a dark brown coloration.

tion, 1 ml of dimethylglyoxime reagent is added. The immediate formation of a bright red precipitate proves the presence of nickel.

Test for Cobalt: One gram of sodium acetate is added to a 2-ml portion of the group solution made just neutral with dilute hydrochloric acid. Two ml of nitroso-R-salt solution is added, the solution boiled; 1 ml of concentrated nitric acid is then added, and the boiling continued for two minutes. A red color will appear if cobalt is present. Copper and nickel also give a color reaction with the nitroso-R-salt reagent, but these colors are destroyed by the nitric acid, while that produced by the cobalt persists. The coloration is attributed to a cobalt-nitroso-R-salt complex.⁵

Test for Zinc: A 3-ml portion of the group solution is acidified with acetic acid and then made basic with 3N sodium hydroxide solution, 1 ml in excess being added. The mixture is centrifuged to separate the insoluble hydroxides of copper, nickel, cadmium and cobalt. The residue is reserved for treatment in the next section in testing for cadmium. To the resulting sodium hydroxide solution, which may contain zinc as the zincate ion, 5 drops of 8-hydroxyquinoline reagent is added. If zinc is present, a heavy yellow precipitate will result.

⁵van Kleoster, H.S., J. Am. Chem. Soc., 43: 746 (1921).

Test for Cadmium: The precipitate of the hydroxides obtained from the sodium hydroxide treatment in the test for zinc above is dissolved in dilute acetic acid. Ammonia is added until the solution is basic to litmus, and then 8-hydroxyquinoline solution is added dropwise. The presence of cadmium is indicated by the formation of a heavy yellow precipitate on the addition of 2 or 3 drops of the reagent.

Test for Copper: If a negative test has been obtained for nickel, a blue solution here indicates the presence of copper. A drop of the solution which may contain copper in the form of the ammonia complex is placed on a filter paper spot plate; then a drop of diphenylthiocarbazone reagent is added to the drop of solution. The greenish color of the reagent becomes a dark brown in the presence of copper.

If positive tests have been obtained for nickel, cobalt, cadmium and zinc, another test may be made for copper. To 2 drops of diphenylcarbazone reagent contained in a depression of a porcelain spot plate is added 1 drop of the ammoniacal test solution. The mixture is agitated with a micro stirring rod for fifteen to twenty seconds. If copper is present, the red color formed immediately will fade completely on stirring, leaving a dark purple-red residue at the edges of the depression, but a colorless solution. The red color will persist in the absence of copper. As little as 2 mg of copper per liter in the presence of the other ammonia complex ions is detectable by this test. Experimental

CHART VII: SCHEME OF ANALYSIS FOR GROUP IV

DIVISION B: The Group IV-B soln may contain AlO_2^- , CrO_2^- , PbO_2^- and SbO_4^{3-} . Individual portions are used in the following tests.

Lead: To 1 ml of test soln add dropwise 1 ml of K_2CrO_4 . A yellow crystalline ppt of PbCrO_4 confirms the presence of Pb^{++} .

Carefully neutralize another 1-ml portion of test soln with HOAc. Now place a drop of the soln on a spot plate with a drop of diphenylthiocarbazone reagent and agitate the mixture with a small stirring rod. In the presence of Pb^{++} the mixture assumes a reddish coloration.

Antimony: Neutralize 1 ml of soln with HOAc and place 1 drop of this soln on a spot plate. Add 2 drops 3N HCl and 1 or 2 small crystals of NaNO_2 . Stir until brown NO_2 fumes cease. Then add 2-3 drops of rhodamine-B reagent. A blue to violet coloration or ppt indicates the presence of Sb^{+++} .

Chromium: Acidify a 2-ml portion with HNO_3 , boil for two minutes and let cool. Five drops of this soln is placed in a porcelain spot plate. Note the reaction carefully as 2 drops of 3 per cent H_2O_2 is added. If Cr^{++} is present, there is formed a blue coloration which may fade rapidly. Add HCl dropwise to a 1-ml portion of the test soln until just slightly alkaline to litmus. Place 5 drops of this soln in a spot plate and add 3-4 drops of benzidine soln, then a drop or two of 3 per cent H_2O_2 . An intense blue color forming immediately confirms the presence of Cr^{+++} .

Aluminum: Make 1 ml of the test soln just acid with HOAc, add 3-4 drops of aluminon reagent, and warm the soln for one minute in a bath of boiling water. Now add NH_4OH till the soln is basic. A reddish gelatinous ppt indicates the presence of Al^{+++} .

evidence shows that this test is valid and most accurate only in the presence of some of the other ammonia complexes.

Section 6B. IDENTIFICATION OF GROUP IV-B

The solution designated as Group IV-B may contain the metals of the amphoteric group as aluminate, chromite, plumbate and antimonite ions.

Test for Lead: To a 1-ml portion of the solution is added dropwise 1 ml of a potassium chromate solution. The presence of lead is indicated by the formation of a bright "chrome yellow" precipitate of lead chromate.

An alternative test for lead may be made by carefully neutralizing a 1-ml portion of the group solution with acetic acid. One drop of the neutral solution is placed on a porcelain spot plate with a drop of diphenylthiocarbazone reagent, and the mixture thoroughly agitated with a small stirring rod. In the presence of lead, the green color of the reagent becomes red against a white background.⁶

Test for Antimony: In the depression of a spot plate 1 drop of a 1-ml portion of the solution which has been neutralized with acetic acid is placed. The solution is made decidedly acid with 3N hydrochloric acid. Then 1 or 2 small crystals of sodium nitrite are added and the mixture thoroughly agitated with a stirring rod until the brownish fumes

⁶Fischer, H., Z. angew. Chem., 42: 1025 (1929).

of nitrogen dioxide are no longer evolved. A violet to blue coagulated precipitate formed on the addition of 2-3 drops of rhodamine-B reagent confirms the presence of antimony.

Test for Chromium: A 2-ml portion of the group solution is acidified with dilute nitric acid, heated in a boiling water bath for two minutes and cooled. Five drops of this solution is placed in a porcelain spot plate and the spot studied carefully as 2 drops of 3 per cent hydrogen peroxide solution is added. The immediate formation of a blue coloration, which may fade rapidly, indicates the presence of chromium.

A further test may be made for chromium by adding dilute hydrochloric acid dropwise to a 1-ml portion of the group solution until the solution reacts just slightly alkaline to litmus. To 5 drops of this solution placed on a spot plate is added 3-4 drops of benzidine solution and a drop or two of 3 per cent hydrogen peroxide solution. An intense blue color confirms the presence of chromium.

Test for Aluminum: A 1-ml portion of the solution believed to contain aluminum is made just acid with acetic acid, 3-4 drops of aluminon reagent is added, and the solution is heated for one minute in a bath of boiling water. A reddish gelatinous precipitate formed when the solution is made basic with dilute ammonium hydroxide shows the presence of aluminum. The colored precipitate is a lake formed by the red dye and the mordant, aluminum hydroxide.

CHART VIII: SCHEME FOR SEPARATION AND ANALYSIS OF GROUP V

To the soln remaining after the removal of Groups III and IV, add a gram of NH_4Cl . Make alkaline with NH_4OH and then add $(\text{NH}_4)_2\text{CO}_3$ soln to complete pptn. Filter. Save filtrate for Group VI analysis. Residue may be Ba^{++} , Sr^{++} , and Ca^{++} as carbonates. Wash with a few ml of hot water and reject the washings. Dissolve ppt in 5 ml of hot HOAc and dilute to 15 ml.

Preliminary Test for Barium:

Add 1 ml of K_2CrO_4 soln to 1 ml of test soln. A yellow ppt of BaCrO_4 shows Ba^{++} present. If test is negative, proceed to the preliminary test for Sr^{++} .

If test shows Ba^{++} present: Add K_2CrO_4 to the remainder of soln to remove Ba^{++} . Filter.

Residue: BaCrO_4 . Wash with hot water. Dissolve in a few drops of 6N HCl . Test in Bunsen flame with platinum wire. A yellow-green coloration confirms presence of Ba^{++} .

Filtrate: Sr^{++} and Ca^{++} as chromates. Reppt as carbonates as above. Dissolve carbonates in 5 ml of HOAc and bring volume to 10 ml with water.

Preliminary Test for Strontium: Add 2 ml of a satd soln of CaSO_4 to a hot 1-ml portion of test soln. A white ppt or cloudiness formed on standing five minutes shows Sr^{++} present. If negative, proceed to test for Ca^{++} .

If test shows Sr^{++} present: Make remainder of soln alkaline with NH_4OH and add $(\text{NH}_4)_2\text{SO}_4$. Boil for two minutes and filter.

Residue: SrSO_4 . Wash with hot water. Test in Bunsen flame with Pt wire. A brilliant crimson coloration confirms Sr^{++} .

Filtrate: May contain CaSO_4 . Place 2-3 drops on watch glass with 5-6 drops of $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ reagent and 2 drops of ethyl alcohol. A white ppt

shows Ca^{++} present. To confirm, add $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the alkaline soln. A white ppt insoluble in HOAc and producing a yellowish-red flame test proves the presence of Ca^{++} .

Section 7. SEPARATION AND IDENTIFICATION OF GROUP V

To the solution designated as Groups V-VI is added a gram of ammonium chloride. Ammonium carbonate solution is then added slowly until precipitation is complete. A precipitate forming at this point may consist of carbonates of barium, strontium and calcium. This is separated by centrifuging, the clear supernatant liquid is decanted into a flask labelled "Group VI," and set aside for later analysis.

Test for Barium: The precipitate is washed with a few milliliters of hot water and the washings are discarded. The precipitate is dissolved in 5 ml of 3N acetic acid, the solution diluted with about 10 ml of water and heated to boiling. A preliminary test for barium is made on a 1-ml portion of this solution by adding dropwise 1 ml of potassium chromate solution. A yellow crystalline precipitate of barium chromate indicates the presence of barium. If the test for barium is negative, the preliminary test for strontium may be carried out immediately.

If a positive test for barium has been obtained, potassium chromate solution is added to the remainder of the solution until precipitation is complete in order to remove the barium as the chromate. The mixture is centrifuged and the supernatant liquid, which may contain strontium and calcium, is decanted. The presence of barium may be confirmed by washing the yellow precipitate with a few milliliters of hot water, and then dissolving it in 2 ml of 6N hydrochloric

acid. The solution is evaporated slowly until only a few drops remain. A flame test is made by dipping a clean platinum wire into the solution and holding the wire in a Bunsen flame. A yellow-greenish coloration confirms the presence of barium.

Test for Strontium: The hot solution left after the removal of barium may contain strontium and calcium. Following the previous procedure, these metals are reprecipitated as the carbonates, dissolved in 5 ml of acetic acid, and the resulting solution diluted with an equal volume of water. A preliminary test for strontium is made by heating a 1-ml portion of the solution to boiling, then adding 2 ml of a saturated solution of calcium sulfate and allowing the mixture to stand for a few minutes. A white precipitate or cloudiness, strontium sulfate, appearing in about five minutes indicates the presence of strontium. If the test for strontium proves negative, the test for calcium is carried out immediately.

If the test for strontium is positive, the other part of the solution is made alkaline with dilute ammonium hydroxide and 8-10 ml of ammonium sulfate is added. The mixture is then boiled for about two minutes, centrifuged, and the clear solution set aside for the calcium test. The white precipitate is strontium sulfate. The presence of strontium is confirmed by picking up a small amount of the residue on a clean platinum wire and holding it in a Bunsen flame for a

CHART IX: SCHEME OF ANALYSIS FOR GROUP VI

The filtrate from Group V may contain Mg^{++} , Na^+ , K^+ , NH_4^+ and some unpptd alkaline earth ions. To remove the latter, add a half-ml each of $(NH_4)_2C_2O_4$ and $(NH_4)_2SO_4$ reagents, heat to boiling, and filter if necessary. If a positive test was obtained in the preceeding group, discard any ppt formed at this point. Test ppt for Group V ions if no positive test was found previously.

To test for Magnesium: Add 4-5 drops of guinalizerin reagent to 2 ml of test soln, then make distinctly basic with NH_4OH . A cornflower blue lake confirms presence of Mg^{++} .

Remainder of soln is evaporated in a casserole under hood till spattering begins. Add conc HNO_3 and repeat evaporation to dryness and heat until fumes of NH_4^+ salts are no longer detectable. A residue indicates Na^+ or K^+ .

Test a portion of residue in flame. A violet coloration shows the presence of K^+ and the absence of Na^+ .

A bright yellow flame lasting at least five seconds indicates Na^+ . If Na^+ is present, examine flame through two thicknesses of cobalt glass just as the wire is introduced into the flame. A red-violet coloration through the cobalt glass indicates K^+ .

If flame tests are doubtful, dissolve residue in 5 ml of water, heating if necessary. Divide into two portions.

Test for Potassium: To one part add 2 ml of hot conc naphthol yellow-S reagent and let stand for ten to fifteen minutes. A flocculent golden yellow ppt confirms the presence of K^+ .

Test for Sodium: Add to the other part, 2 ml of glacial $HOAc$ and 1 ml of zinc uranyl acetate reagent. Shake well and let stand for ten minutes. The presence of Na^+ is proved by a yellow crystalline ppt.

To test for Ammonium: A 5 ml-portion of the original soln is placed in a beaker and made distinctly alkaline with 6N $NaOH$, added slowly with stirring. The beaker is covered with a small watch glass on the under side of which is placed a moistened piece of red litmus paper. Warm the mixture cautiously to avoid spattering; do not boil. A uniform change in the litmus to blue, without any deep blue spots, shows NH_4^+ to be present.

minute or two. The wire is then dipped in concentrated hydrochloric acid and returned to the flame. The presence of strontium is indicated by a brilliant crimson coloration.

Test for Calcium: Two or three drops of the solution which may contain calcium is placed on a watch glass, then 5-6 drops of ammonium ferrocyanide reagent and 2 drops of ethyl alcohol are added. A white precipitate, readily discernible against a dark background, indicates the presence of calcium.⁷

A confirmatory flame test may be made for calcium, if desired, by adding 5-10 ml of ammonium oxalate reagent to the alkaline solution believed to contain calcium, and noting the formation of a white crystalline precipitate. The precipitate of calcium oxalate is insoluble in acetic acid. A yellowish-red colored flame test proves the presence of calcium.

Section 8. . IDENTIFICATION OF GROUP VI

To the Group VI solution, which may contain the ions magnesium, sodium, potassium and ammonium, are added a half-ml each of ammonium oxalate and ammonium sulfate reagents to insure complete removal of the alkaline earth ions. The solution is heated to boiling and centrifuged if a precipitate is formed. If no positive tests have been obtained in the previous group, a series of flame tests is run, using the

⁷Feigl, F., and Pavelka, F., Mikrochemie, 2: 85 (1924).

precipitate as directed in Section 7. The precipitate is discarded if any of the tests was positive. The solution is tested for the Group VI ions.

Test for Magnesium: Four or five drops of quinalizarin reagent is added to 2 ml of the test solution, and then ammonium hydroxide is added to distinct basic reaction. The presence of magnesium is confirmed by the formation of a cornflower blue adsorption lake.⁸

The remainder of the solution is placed in a small casserole or evaporating dish and evaporated under a hood until spattering just begins. Five to ten ml of concentrated nitric acid is added and the evaporation repeated, carrying the solution to dryness. The residue is further heated on the sides of the dish as well as on the bottom, until no more fumes of ammonium salts are given off. The dish is allowed to cool.

Tests for Sodium and Potassium: A tiny particle of the solid residue is taken up on the end of a clean platinum wire moistened with hydrochloric acid and held in the flame. A violet coloration shows the presence of potassium and the absence of sodium. A bright yellow coloration in the flame persisting for at least five seconds indicates the presence of sodium. If sodium is present, the test for potassium must be repeated, viewing the flame through several thicknesses of

⁸Hahn, F.L., Wolf, H., and Jäger, G., Ber., 57: 1394 (1924).

cobalt glass in order to filter out the sodium and Bunsen flames. In this test, the color of the flame is observed at the instant the wire is introduced into the flame. The potassium flame will appear violet through the cobalt glass.

If the results of the flame tests are doubtful, the remainder of the residue is dissolved in 5 ml of water in the casserole with heat, if necessary. This solution is divided into two portions.

To one part, 2 ml of a hot concentrated solution of naphthol yellow-S (2 per cent) is added, and the reaction tube allowed to stand for ten to fifteen minutes. The formation of a flocculent golden yellow precipitate is an indication of the presence of potassium.⁹

To the other part are added 2 ml of glacial acetic acid and 1 ml of zinc uranyl acetate reagent, the tube thoroughly shaken and set aside and allowed to stand for about ten minutes. The presence of sodium is proved by the formation of a yellow crystalline precipitate, sodium zinc uranyl acetate.¹⁰

Test for Ammonium: This test must be made on a portion of the original test solution. Five ml of test solution is placed in a small beaker and 6N sodium hydroxide added

⁹Clark and Willits, Ind. Eng. Chem., Anal. Ed., 8: 202 (1936).

¹⁰Kolthoff, I.M., Z. anal. Chem., 70: 398 (1927).

with constant stirring until the mixture is strongly alkaline. A piece of moistened red litmus paper is placed on the convex side of a small watch glass which is then placed convex side down over the beaker. The solution is warmed very gently, but not boiled. If ammonium is present, the color of the litmus will change uniformly from red to blue, without the formation of any deep blue spots.

V. SPECIAL REAGENTS AND MATERIALS

Aluminon: A 0.1 per cent aqueous solution.

Ammonium Ferrocyanide: A saturated aqueous solution.

Ammonium Molybdate: Dissolve 10 g of molybdic oxide in a mixture of 30 ml of distilled water and 15 ml of concentrated ammonium hydroxide. Add this solution slowly and with constant stirring to a mixture of 50 ml of concentrated nitric acid and 115 ml of water.

Ammonium Thiocyanate: A 10 per cent aqueous solution.

Benzidine: Dissolve 2 g of benzidine in 100 ml of 3N acetic acid.

Dimethylglyoxime: One gram in 100 ml of ethyl alcohol.

Diphenylamine: One gram in 100 ml of ethyl alcohol.

Diphenylcarbazone: Dissolve 0.5 g in 100 ml of ethyl alcohol.

Diphenylthiocarbazone: Ten mg in 100 ml of carbon tetrachloride.

8-Hydroxyquinoline: Dissolve 4 g in 10 ml of acetic acid and dilute to 100 ml with water.

Naphthol Yellow-S: A 2 per cent aqueous solution. Heat 2 g in 100 ml of water until dissolved.

Nicotine-Thiocyanate Reagent: Dissolve 20 g of pure ammonium thiocyanate in 50 ml of distilled water. Add 20 ml of 99 per cent nicotine alkaloid and bring volume to 100 ml with distilled water.

Nitroso-R-Salt: A 0.5 per cent aqueous solution.

Potassium Ferrocyanide: A 10 per cent aqueous solution.

Pyridine: A 20 per cent aqueous solution. Dissolve 20 ml of pure pyridine in 80 ml of distilled water.

Pyridine-Thiocyanate Reagent: Dissolve 10 g of pure ammonium thiocyanate in 90 ml of water and add 10 ml of pure pyridine.

Quinalizarin: Dissolve 1 mg in 100 ml of ethyl alcohol.

Rhodamine-B: Ten mg in 100 ml of water.

Zinc Uranyl Acetate: Dissolve 5 g of uranyl acetate with 3 ml of warm 30 per cent acetic acid and bring volume to 25 ml with water. Mix 15 g of zinc acetate with 3 ml of 30 per cent acetic acid and dilute to 25 ml. Combine these two solutions, warm, add 0.1 g of sodium chloride, allow mixture to stand overnight, and filter.

Preparation of Filter Paper Spot Test Plates: These spot plates are made with the aid of a printing block patterned after one designed by Yagoda.¹ The printing tool consists of a block of cast iron, or some other suitable metal, 2 x 4 x 0.5 inches in size, with smooth polished surfaces. A total of 15 half-inch holes are drilled into the face of the block to a depth of about one-fourth inch. The handle is of wood and is detachable.

¹Yagoda, H., Ind. Eng. Chem., Anal. Ed., 9: 79 (1937).

The block, with handle detached, is warmed for a few minutes on a hot plate or in an oven at a temperature of 70° C for best results. A piece of ordinary 11-cm filter paper is placed on a flat block of paraffin and the heated tool is then pressed firmly on the paper for a few seconds. The tool is raised and the paraffined paper quickly and carefully removed from the block of paraffin. With a little practice, the most suitable technique can be developed and repeated as often as desired to make a supply of the test plates.

The resulting test plate is a paraffined paper with 15 half-inch circular areas untouched by paraffin. The paraffin-bounded spots are then impregnated by placing a drop of the specified reagent in the center and allowing the spot to dry. After the paraffining process, the sides of the filter paper spot plates may be folded at the edge of the paraffin in such a manner as to furnish a support while drying after the impregnation with the reagent.

BIBLIOGRAPHY

- Clark, A.W., and C.O. Willits, Industrial and Engineering Chemistry, Analytical Edition, 8: 209, 1936.
- Curtman, L.J., Qualitative Chemical Analysis, New York: Macmillan, 1938. 514 pp.
- Dobbins, J.T., E.C. Markham and H.L. Edwards, Journal of Chemical Education, 16: 94-98, February, 1939.
- Feigl, F., Mikrochemie, 1: 12, 1923.
- _____, Specific and Special Reactions for Use in Qualitative Analysis, New York: Elsevier, 1940. 192 pp.
- _____, and F. Pavelka, Mikrochemie, 2: 85, 1924.
- Fischer, H., Zeitschrift fur angewandte Chemie, 42: 1025, 1929.
- FitzGibbon, M., British 492,660, September 20, 1938.
- Hahn, F.L., H. Wolf and G. Jäger, Berichte der deutschen chemischen Gesellschaft, 57: 1394, 1924.
- Jackson, K.E., Chemical Reviews, 29: 123-197, August, 1941.
- Klemenc, A., and F. Pollack, Zeitschrift fur anorganische und allgemeine Chemie, 115: 131-140, 1921.
- Kolthoff, I.M., Zeitschrift fur analytische Chemie, 70: 398, 1927.
- _____, and W. Bosch, Recueil des travaux chimiques des Pays-Bas, 48: 37-48, 1929.
- _____, and G.E. Noponen, Journal of the American Chemical Society, 55: 1448, 1933.
- Liquier, J., Annales de physique, 8: 121-203, 1927.
- Wellan, Ibert, Organic Reagents in Inorganic Analysis, Philadelphia: Blakiston, 1941. 682 pp.
- Morgan, G.T., and H.D.K. Drew, Journal of the Chemical Society, 117: 1456, 1920.

- Prodinger, W., Organic Reagents Used in Quantitative Inorganic Analysis, New York: Elsevier, 1940. 203 pp.
- Schmidt, J., and V. Hinderer, Berichte der deutschen chemischen Gesellschaft, 65: 87, 1932.
- van Klooster, H.S., Journal of the American Chemical Society, 43: 746, 1921.
- Yagoda, H., Industrial and Engineering Chemistry, Analytical Edition, 9: 79 (1937).
- Yoe, J.H., and L.A. Sarver, Organic Analytical Reagents, New York: Wiley and Sons, 1941. 339 pp.